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A study on the morphology of polystyrene-grafted poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) films prepared using a simultaneous radiation grafting method

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HIGHLIGHTS

- PS-grafted ETFE films were prepared by a simultaneous radiation grafting method was investigated.
- The natural crystalline structures of grafted ETFE films are not affect by the degree of grafting.
- The inter-crystalline distance of the ETFE films increase with increasing degree of grafting.
- The styrene monomers are mainly grafted on the ETFE amorphous regions during a simultaneous radiation grafting using gamma-ray.

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ABSTRACT

The morphology of polystyrene-grafted poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) films prepared using a simultaneous radiation grafting method was investigated using DMA, DSC, XRD, and SAXS instruments. The DMA study indicates that the ETFE amorphous phase and PS amorphous phase are mixed well in the PS-grafted ETFE films while the ETFE crystalline phase and the PS amorphous phase are separated, suggesting that the PS chains are grafted mainly on the ETFE amorphous regions. The DSC and XRD data showed that the natural crystalline structures of ETFE in the grafted ETFE films are not affected by the degree of grafting. The SAXS profiles displayed that the inter-crystalline distance of the ETFE films increases with an increasing degree of grafting, which further implies that the PS graft chains formed by the simultaneous irradiation has a significant impact on the amorphous morphology of the resulting grafted ETFE film. Thus, these results indicate that the styrene monomers are mainly grafted on the ETFE amorphous regions during the simultaneous radiation grafting process.

1. Introduction

Graft copolymerization is a useful method for modifying some of the important properties of natural and synthetic polymers (Nasef et al., 2004). A wide range of research on the graft copolymerization of commercial polymer with vinyl or acryl monomers has already been conducted. Compared to other grafting methods, radiation grafting has been researched for several decades owing to its many unique advantages such as high reactivity, deep penetration ability, and fast processing time. Irradiation grafting can be conducted by two different methods, pre-irradiation and simultaneous irradiation (Gürsel et al., 2008). In a pre-irradiation method, polymer is irradiated either in the absence of air or in the presence of air to make radicals on the polymer backbone prior to the reaction with a grafting monomer (two step reaction). However, in a simultaneous irradiation method, the radical formation on the polymer backbone and grafting process occur simultaneously when a mixture of a base polymer and a grafting monomer is subjected to irradiation (single step reaction).

Gürsel et al. (2008) examined the effects of the reaction conditions on the grafting of styrene onto ETFE films using a pre-irradiation process. In his work, the rate and extent of grafting were found to be significantly dependent on the grafting conditions. In addition, Walsby et al. (2001) disclosed that the grafting of styrene onto different base fluoropolymers yielded different degrees of grafting under the same pre-irradiation conditions. It was also found that the degree of grafting is largely affected by the formed radicals, polymer structure, and its crystallinity. Recently, Shin et al. reported the distribution behaviors of polystyrene sulfonic acid (PSSA)-grafted over the cross-section of grafted PFA membranes on the basis of a SEM-EDX analysis (Shin et al., 2009).

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It was observed that the distribution behaviors were largely affected by the grafting conditions such as the degree of grafting, monomer concentration, and film thickness.

In previous studies, the morphology of crystalline for PS-grafted fluoropolymer films prepared using a pre-irradiation grafting method has been mainly investigated using DSC, XRD, SAXS, and SANS instruments (Balog et al., 2010, 2011, 2012; Youncef et al., 2008, 2010; Brack et al., 2000; Nasef et al., 2010). Iwase et al. (2011) investigated the pre-irradiation graft polymerization of styrene on a crosslinked poly(tetrafluoroethylene) (PTFE) film on the basis of time-resolved SANS. It was observed that the graft polymerization occurs at an interface of the PTFE microcrystal, and a thin layer of PS graft chains is formed surrounding the fluoropolymer microcrystal. Mortensen et al. reported small-angle neutron studies of PS-grafted FEP films prepared using a pre-irradiation method (Mortensen et al., 2008). It was found that the degree of crystalline domain of the original fluoropolymer films was decreased with an increasing degree of grafting. Nasef and Hegazy (2004) investigated the pre-irradiation graft polymerization of styrene monomer on poly (vinylidene fluoride) (PVDF) films (Nasef et al., 2004). It was observed that with an increase in the degree of grafting, the melting temperature of the PS-grafted PVDF films was shifted to a low temperature, indicating that the degree of crystalline in the PVDF films was reduced after pre-irradiation graft polymerization.

Interestingly, the morphology of PS-grafted fluoropolymer film prepared through a simultaneous irradiation method has not been studied in detail. In this study, we prepared PS-grafted ETFE films using a simultaneous radiation grafted method, and investigated their dynamic mechanical properties using DMA, and the morphology of the crystalline domain using XRD, DSC, and SAXS. The dynamic mechanical properties of the PS-grafted ETFE films were also correlated with the morphology results.

2. Experimental

2.1. Materials

An ETFE film (100 μm thickness) was obtained from Ashahi Glass Co. Ltd. Styrene monomer (99%) was purchased from Showa Co. and used as received. Other chemicals including the solvents were of reagent grade and used without further purification.

A simultaneous irradiation method was used in this experiment for the grafting of styrene onto ETFE film. A quantity of 100 μm ETFE films were cut into 6 cm × 60 cm in size and immersed in a styrene monomer/dichloromethane (60/40, v/v) mixture. The mixtures containing ETFE films were purged with nitrogen for 10 min and irradiated by γ-ray from the ^{60}Co source at a dose rate of 2 kGy/h. The irradiation films were washed with dichloromethane for 24 h and dried in a vacuum oven for 12 h at 60 °C. The degree of grafting (DOG) was calculated as below,

$$\mathrm{DOG}(\%) = [(W_g - W_o)/W_o] \times 100 \quad (1)$$

where W_g is the weight of the film after grafting, and W_o is the weight of the film before irradiation. The degree of grafting of the film was 29%, 37%, 42% and 66%, respectively.

2.2. Mechanical and thermal properties

A dynamic mechanical analysis of ETFE and ETFE-g-PS films was performed on a TA DMA Q800 (TA Instruments, USA). The experiments were carried out in a tensile mode at 1 Hz from −100 °C to 300 °C with a heating ramp of 2 °C/min. Storage modulus (E') and loss tangents (tanδ) were obtained as a function of temperature. For each sample, a detailed analysis of the tanδ peaks was carried out using Peakfit software (SPSS, Inc.).

2.3. Differential scanning calorimetry (DSC)

DSC data were collected using a TA differential scanning calorimeter (DSC 2000). The PS-grafted samples were dried at 70 °C under a vacuum for 12 h prior to thermal analysis. The samples (ca. 10 mg) were scanned from −50 °C to 350 °C at a rate of 10 °C/min under a N_2 atmosphere.

2.4. X-ray diffraction (XRD)

An XRD experiment was performed using a **PANalytical** X'pert PRO MPD X-ray diffractometer (Almelo, Netherland). A sealed tube source was used to produce the Cu $K\alpha$ radiation ($\lambda = 1.54$ Å) and the sample-to-detector distance was fixed to 10 cm, which allowed XRD data to be obtained in the 2 theta from ca. 10° to 50°. The power of the X-ray generator was set to be 40 kV and 30 mA. The scanning speed used was 1 °/min, and the sampling width was 0.05°.

2.5. Small angle X-ray scattering (SAXS)

A SAXS experiment was performed using the Pohang Accelerator Laboratory II (PAL II) synchrotron radiation source (Pohang, Korea) at station 4C. The incident X-ray beam was tuned to a wavelength of 0.675 Å, and the sample-to-detector distance was fixed to 4018 cm. The two-dimensional scattering patterns were recorded on a high resolution Mar CCD camera with a 30 s exposure time. The SAXS data were plotted as the relative intensity versus scattering vector q after correction for sample absorption and background, where $q = 4\pi \sin\theta/\lambda$, θ is half the scattering angle, and λ is the X-ray wavelength.

3. Results and discussion

Fig. 1 shows the storage modulus and loss tangent values of the pure ETFE and PS-grafted ETFE films as a function of temperature. The storage modulus for pure ETFE film shows a broad glass transition point at about 60 °C, and the film shows a rubbery modulus. Above 220 °C, the sample starts to flow, and for the PS-grafted ETFE films, the modulus curve shows a very similar behavior to the pure ETFE films with increasing temperatures. It was found that the position of a sharp drop in a modulus curve from a glass transition temperature at 120 °C does not change much with an increase in the degree of PS grafting. Above the glass transition temperature, however, the modulus curve moves to a lower value upon an increasing degree of grafting.

The loss tangent curves for the ETFE precursor and PS-grafted ETFE films can be seen in Fig. 1. Two loss tangent peaks, a shoulder like peak at ca. 60 °C and a peak at ca. 92 °C, were observed from the pure ETFE films. Ono et al. (2011) reported that the shoulder like tanδ peak is a crystal-crystal transition from an orthorhombic to hexagonal form of ETFE (ETFE $T_{g,1}$) and the higher temperature tangent peak is a typical glass transition temperature of the ETFE amorphous regions (ETFE $T_{g,2}$) (Ono et al., 2011). For the PS-grafted ETFE films, the loss tangent plots show that there are three tanδ peaks: two shoulder link peaks at low temperature are due to the glass transition temperature of the ETFE regions, whereas the other at a high temperature peak is due to the glass transition temperature of the PS regions. The size of the ETFE peak decreases, while that of the PS peak increases with an increasing degree of grafting. Therefore, it can be concluded that the PS chains are grafted mainly on the ETFE amorphous regions.